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GRAIN BOUNDARY ENERGETICS IN NON-OXIDE CERAMICS.(U)  
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Grain Boundary Energetics in  
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### Abstract

Research on "Grain Boundary Energetics in Non-Oxide Ceramics" has been conducted at CWRU since 1975 has concentrated on two specific areas--the  $\beta \rightarrow \alpha$  transformation in polycrystalline SiC, and the nature of grain boundary phases in hot-pressed  $\text{Si}_3\text{N}_4$  containing various densification aids.

The  $\beta \rightarrow \alpha$  transformation in polycrystalline SiC is unusual in that it appears to occur in two stages. The first involves the growth of composite plates consisting of  $\alpha$ -SiC plates sandwiched between recrystallized envelopes of  $\beta$ -SiC. This stage ends when the original polycrystalline  $\beta$  matrix is consumed. The second and more sluggish stages involves the thickening of the  $\alpha$  plates within their  $\beta$  envelopes and requires repeated piecewise nucleation of  $\alpha$  at the  $\beta \rightarrow \alpha$  interface.

High resolution TEM has been used to show that commercial MgO-doped hot-pressed  $\text{Si}_3\text{N}_4$  apparently contains a continuous grain boundary phase that is responsible for the poor high-temperature performance. Grain boundary microstructures have been characterized in polycrystalline  $\text{Si}_3\text{N}_4$  containing  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{BeSiN}_2$ ; the latter additive appears to be the most promising, since a continuous grain boundary film is not present.

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### Summary of Results

Research on "Grain Boundary Energetics in Non-Oxide Ceramics" was conducted by Professors A.H. Heuer and T.E. Mitchell of the Department of Metallurgy and Materials Science at Case Western Reserve University (CWRU) during the period 1 February, 1978 to 31 January, 1978. This section of the Final Technical Report summarizes the achievements of this work. The research began with two questions in mind: i) was the ratio of grain boundary to surface energies ( $\gamma_{GB}/\gamma_{SV}$ ) too high in undoped SiC and other non-oxide ceramics to permit pressureless sintering to proceed to high sintered densities? and ii) what was the importance of dislocation creep relative to grain boundary sliding (GBS) creep during high temperature deformation in  $Si_3N_4$ ? One important feature of the proposed work was the heavy reliance of transmission electron microscopy (TEM).

Both topics were attacked with vigor during the early stages of the research and qualitative answers to the two questions appeared rather quickly. The difficulty of sintering non-oxide ceramics is not due to a too high value of  $\gamma_{GB}/\gamma_{SV}$ , and hence a low value of the dihedral angle at a pore-grain boundary intersection, as the initial results showed that dihedral angles were  $\geq 100^\circ$  in SiC. In the case of crept  $Si_3N_4$  (samples obtained from Battelle Columbus Laboratories), the initial results suggested that GBS was much more dominant than dislocation creep in state-of-the-art, commercial (e.g. HS-130 and NC-132) hot-pressed  $Si_3N_4$ .

During the course of the TEM studies that led to these qualitative conclusions, two important questions suggested themselves for study and these became the main topics of research during the grant period. Each will be discussed in turn.



### $\beta \rightarrow \alpha$ Transformation in Polycrystalline SiC

Polycrystalline  $\beta$ -SiC (i.e. the cubic polymorph) transforms upon annealing at temperatures above  $\sim 1800^\circ\text{C}$  to the  $\alpha$  form-- $\alpha$  being the collective designation of a large number of polytypes with hexagonal or rhombohedral symmetry, all based on different stacking sequences of the basic Si-C double layer. The mechanism of this transformation is of considerable technological importance since the  $\alpha$  transformation product invariably appears as large platelets which degrade the mechanical properties. A noteworthy and unique feature of the  $\beta \rightarrow \alpha$  transformation in polycrystalline SiC is the fact that these  $\alpha$  plates are "sandwiched" between "sheaths" or "envelopes" of recrystallized  $\beta$ -SiC.

It appears that transformation occurs in two conceptually-distinguishable stages: the first involves the growth of these composite plates until the original polycrystalline matrix is completely consumed, and the second (and much more sluggish) stage is the thickening of the  $\alpha$  plates within their  $\beta$  sheaths.

This unusual morphology of the reaction product and unusual transformation sequence arises from the fact that the interface between the  $\alpha$  plate and the  $\beta$  sheath involves parallel close packed planes in both phases ( $\{111\}_\beta \parallel \{0001\}_\alpha$ ) and the resulting interfacial energy appears to be several orders of magnitude less than high angle  $\beta/\beta$  or  $\alpha/\alpha$  grain boundaries or randomly-oriented  $\beta/\alpha$  interface boundaries. The sluggishness of the final stages of the  $\beta \rightarrow \alpha$  transformation follows directly from the very low energy of the  $(\{111\}_\beta / \{0001\}_\alpha)$  coherent interface and the subsequent need for repeated piecewise nucleation of  $\alpha$ --an  $\alpha$  nucleus can propagate rapidly parallel to the  $\beta/\alpha$  interface but cannot grow easily perpendicular to this interface.

The first stage of the transformation is discussed in papers 2 and 3 in Table I, which is a list of publications arising from this research, while the final stage is treated in paper 4. In addition, the microstructure of sintered polycrystalline  $\alpha$ -SiC (produced by Carborundum Co.) with respect to the polytypes and impurity phases present has been characterized by TEM and the results are being written up for publication (paper 5 in Table I.)

#### Grain Boundary Phase(s) in $\text{Si}_3\text{N}_4$

The presence of a continuous grain boundary film in hot-pressed  $\text{Si}_3\text{N}_4$  has been suspected since the discovery more than 5 years ago that serious (and unacceptable) loss in strength took place at  $\sim 1400^\circ\text{C}$ . While the notion that this weakening resulted from softening and flow of a MgO-containing (presumably silicate) phase present because of the MgO added to permit liquid-phase densification during hot pressing, direct micrographic evidence of this phase was not available in commercial materials, in spite of the prior TEM work addressed to this point. As discussed in papers 1 and 6 in Table I, both HS-130 and NC-132 appear to have a continuous grain boundary phase (in addition to measurable amounts of  $\text{Si}_2\text{N}_2\text{O}$ , WC, SiC, etc.) but its detection is quite difficult--in electron transmission, the plane of the grain boundary must be accurately parallel to the electron beam and the two grains on either side of the boundary must be oriented such that both are strongly diffracting. Our recent work has involved characterizing microstructures of  $\text{Si}_3\text{N}_4$  fabricated using densification aids other than MgO and will now be summarized.

In order to improve the creep and oxidation resistance of hot-pressed  $\text{Si}_3\text{N}_4$ , a number of additives have been used in place of MgO as densification

TABLE I

Publications and Dissertations resulting from research on  
"Grain Boundary Energetics in Non-Oxide Ceramics"

Publications

- 1 "Lattice Resolution Studies of Engineering Ceramics:  
SiC and  $\text{Si}_3\text{N}_4$ ", A.H. Heuer, L.K.V. Lou, L.U. Ogbuji  
and T.E. Mitchell, J. de Micro. et de Spec. Electron,  
2 (475-480) (1977).
- 2 "The  $\beta \rightarrow \alpha$  Transformation in Polycrystalline Silicon  
Carbide (SiC):  
I - Microstructural Aspects", A.H. Heuer, G.A. Fryburg  
L.U. Ogbuji, T.E. Mitchell and S. Shinozaki, in  
press, J. Amer. Cer. Soc.
- 3 "The  $\beta \rightarrow \alpha$  Transformation in Polycrystalline Silicon  
Carbide (SiC):  
II - Interfacial Energetics", T.E. Mitchell, L.U. Ogbuji  
and A.H. Heuer, in press, J. Amer. Cer. Soc.
- 4 "The  $\beta \rightarrow \alpha$  Transformation in Polycrystalline Silicon  
Carbide (SiC):  
III - Final Stages", L.U. Ogbuji, A.H. Heuer and T.E.  
Mitchell, in preparation.
- 5 "Electron Microscopical Characterization of Sintered  $\alpha$ -SiC",  
L.U. Ogbuji, T.E. Mitchell and A.H. Heuer, in preparation.
- 6 "Impurity Phases in Hot-Pressed MgO-doped  $\text{Si}_3\text{N}_4$ ", L.K.V. Lou,  
T.E. Mitchell and A.H. Heuer, in press, J. Amer. Cer. Soc.
- 7 "Grain Boundary Structures in  $\text{Si}_3\text{N}_4$  Fabricated with  $\text{Y}_2\text{O}_3$ ,  
 $\text{ZrO}_2$  and  $\text{BeSiN}_2$  Additives", K.K.V. Lou, A.H. Heuer and  
T.E. Mitchell, in preparation.
- 8 "Microstructural Changes in  $\text{Si}_3\text{N}_4$  During High Temperature  
Annealing", L.K.V. Lou, T.E. Mitchell and A.H. Heuer,  
in preparation.

Dissertation

- 1 "The Mechanism of the  $\beta \rightarrow \alpha$  Phase Transformation in Silicon  
Carbide: An Electron Microscope Study", L.U. Ogbuji,  
M.S. Thesis (1977).



aids-- $\text{Y}_2\text{O}_3$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{BeSiN}_2$ --and all have been successful in allowing fully-dense bodies to be produced which showed some improvements in properties.  $\text{Y}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  have been chosen in an attempt to produce a more refractory glass phase ( $\text{Y}_2\text{O}_3$  also has the possibility of improving oxidation resistance by forming a stable silicate second phase ( $\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$  in the  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$ - $\text{SiO}_2$  system)).  $\text{ZrO}_2$  has been used in an attempt to improve the toughness while  $\text{BeSiN}_2$  was used with the hope of vitiating the glassy second phase--it is possible to incorporate the additive (subsequent to densification) as a solid solution in  $\text{Si}_3\text{N}_4$ . Without going into the details of recent findings by other workers, the importance of the microstructure of these bodies cannot be dismissed and in particular, the grain boundary structures, which control high temperature behavior, are of paramount interest.

Our recent results are summarized in Table II and will be amplified by the following comments:

1) The stable oxy-nitride in NCX-34 is a yttrium-silicate-oxy-nitride (silicon oxy-nitride is stable in the  $\text{MgO}$  and  $\text{ZrO}_2$  systems, which implies that Mg- and Zr- silicate - oxy-nitrides do not exist.) The presence of large amounts of glassy phases in the G.E. and AMMRAC samples was unexpected, as stable oxy-nitrides are known to exist in both systems.

2) As has already been discussed,  $\text{Si}_3\text{N}_4$  bodies fabricated with  $\text{MgO}$  have a continuous grain boundary film between  $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ ,  $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$  and  $\text{Si}_2\text{N}_2\text{O}/\text{Si}_2\text{N}_2\text{O}$  grains, but the grain boundary film in NCX 34 is apparently restricted to  $\text{Si}_3\text{N}_4/\text{Y}_{10}\text{Si}_4\text{O}_{23}\text{N}_4$  interfaces. In the  $\text{Si}_3\text{N}_4$ - $\text{ZrO}_2$  samples, the grain boundary film is thicker and very extensive, which is probably caused by the low purity starting powders in this body.

TABLE II

Phases found in T.E.M.

Additive	Nitride	Oxynitride	Oxide	SiC	WC	Grain Boundary Film
Norton						
HS 110						
HS 130	$\beta\text{Si}_3\text{N}_4$	$\text{Si}_2\text{N}_2\text{O}$	----	✓	✓	Continuous Film
NC 132						
Norton						
NCX 34	$\beta\text{Si}_3\text{N}_4$	$\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$	----	✓	----	Some
(Max Planck Inst.) N. Claussen 18% $\text{ZrO}_2$	$\beta\text{Si}_3\text{N}_4$	$\text{Si}_2\text{N}_2\text{O}$	$\text{ZrO}_2$	✓		?
G. Gazza (AMRC)	$\beta\text{Si}_3\text{N}_4$	----	Glass----			
S. Prochaska (G.E.)	$\beta\text{Si}_3\text{N}_4$	Much Glass at Triple Points				Very little

3) The G.E. samples offer the most encouraging results. They were fabricated by hot-pressing at  $1850^{\circ}\text{C}$  or sintering at  $2000^{\circ}\text{C}$  under 80 atmospheres of nitrogen. Despite the presence of a large amount of glass at triple points, this glass did not penetrate into the grain boundaries. Among the many grain boundaries investigated, we have only succeeded in finding one grain boundary which was wet by this second phase, and even in this case, the apparent thickness of the film was very thin (less than  $10^{\circ}\text{\AA}$ ). Recent experiments by Drs. Greskovich and Prochazka at G.E. have shown that these materials have excellent properties, i.e. they retain 70% of their room temperature strength at  $1500^{\circ}\text{C}$  and also exhibit excellent oxidation resistance, a result attributable to the high purity of the starting powders. These good high temperature properties are consistent with our observations of the grain boundary structures. These results, as well as summaries of recent studies of microstructural changes occurring in MgO-doped  $\text{Si}_3\text{N}_4$  upon high temperature ( $\sim 2000^{\circ}\text{C}$ ) annealing, are presently being written up for publication papers (7 and 8 in Table I).

#### Personnel

The work on SiC described above has constituted the graduate work of Mr. Linus Ogbuji. He has already obtained an M.S. degree based on some of the results and portions of his Ph.D. thesis will consist the remainder of his SiC work. The research on  $\text{Si}_3\text{N}_4$  has been performed by several post-doctoral research fellows, Drs. B.J. Pletka, G. Das and L.K.V. Lou, with the bulk of the work being performed by Dr. Lou.

Extensive interactions have been maintained with many other workers also studying non-oxide ceramics. These include (in alphabetical order) Drs. Ashbrook (NASA-Lewis), Clake (Rockwell International), Clausen (Max Planck Institute, Stuttgart, W. Germany), Frieman (Naval Research Laboratory),

Graham (Wright-Patterson Air Force Base), Greskovich (G.E.), Prochaska (G.E.), Shinozaki (Ford), Smeltzer (Battelle Labs, Columbus) and Smoak (Carborundum).

Final Comments

The authors would finally like to acknowledge AFOSR, particularly the contract monitor, Major Simmons, for providing the unfettered support for basic studies that have such obvious technological evidence.



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